Density Functional Theory - Levy-Lied Constrained Search Formulation

Lecture 28

CHM 652 / PHY 626
Electronic Structure of Materials

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Lecture Plan

- *N* and *v* representable densities
- Levy-Lieb constrained search formulation of DFT

v representable densities

In deriving the Hohenberg-Kohn theorems we implicitly assumed that the densities of interest can be obtained by applying some external potential to an *N*-electron system. This was crucial in deriving the universal functional as well as the variational principle.

Densities associated with antisymmetric *N*-electron ground state wavefunctions of a Hamiltonian that includes an external potential are termed as *v-representable densities.*

Since F_{HK} is derived from such a wave function, it is also a functional of v-representable densities. That is, the variational principle is only valid for such densities.

Not all valid densities are necessarily *v-representable.*

N representable densities

Densities that are derived from any antisymmetric *N*-electron wavefunction are termed as *N-representable densities.*

Mathematically such densities satisfy (see Parr and Yang)

$$n(\mathbf{r}) \geq 0, \quad \int n(\mathbf{r}) d^3r = N, \quad \int \left| \nabla n(\mathbf{r})^{\frac{1}{2}} \right|^2 d^3r < \infty$$

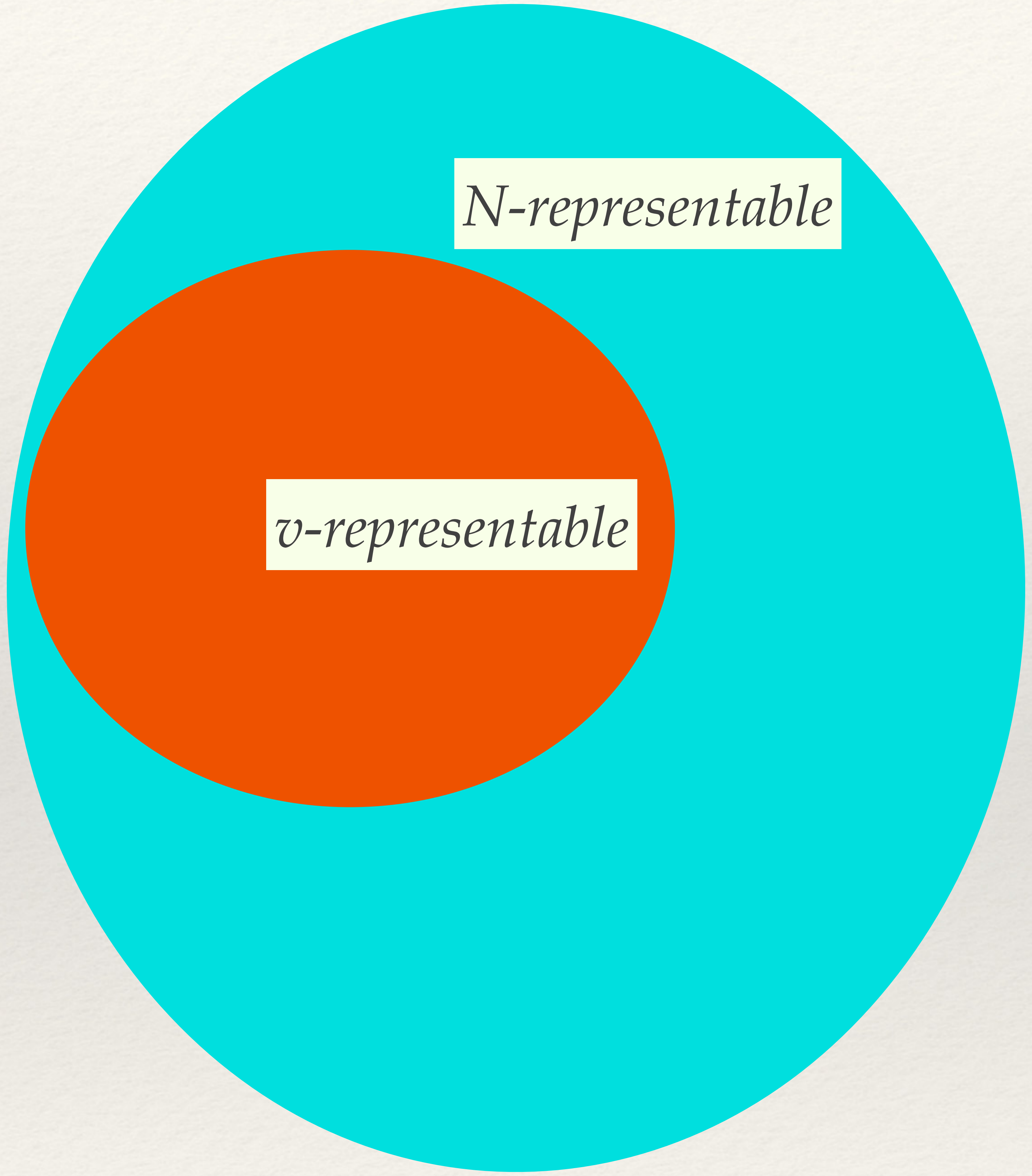
This is a weaker condition.

Pure-state representable : densities obtained from a ground state antisymmetric wavefunction (same as *v-representable*).

Non-interacting pure-state representable : As above except that the Hamiltonian has no interaction among the electrons.

Mixed-state representable : densities obtained by mixing *pure-state* densities.

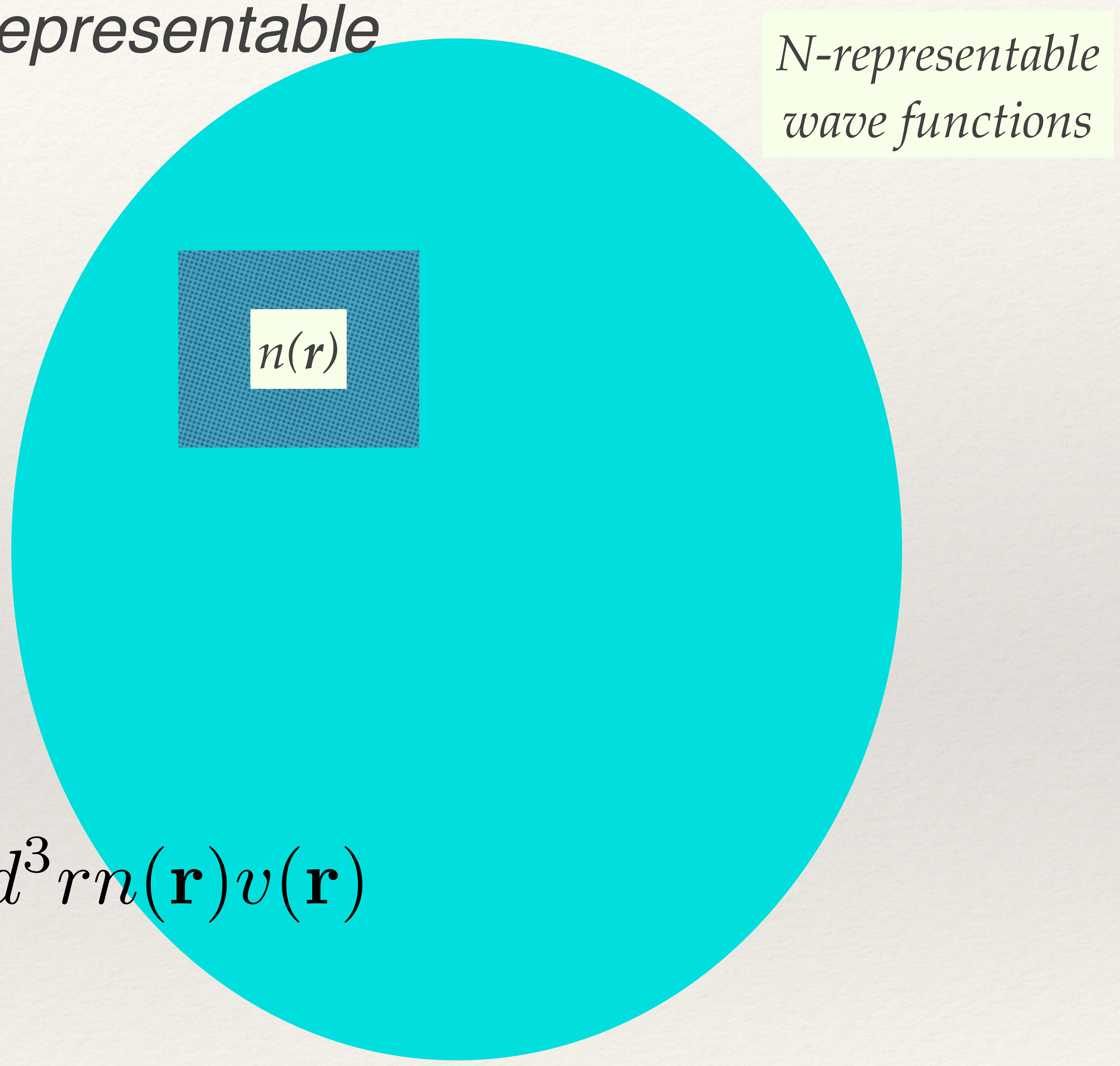
N and v representable wavefunctions



Levy constrained search formulation

The variation principle suggests a search over the *N-representable* space

$$E_0 = \min_{\Psi} \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle$$



Suppose, we break this search into two steps.

1) Search for the minimum over a wave functions yielding a given density n(**r**)

$$\begin{aligned} E[n] &= \min_{\Psi \to n(\mathbf{r})} \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle \\ &= \min_{\Psi \to n(\mathbf{r})} \left\langle \Psi \middle| \hat{T} + \hat{W} \middle| \Psi \right\rangle + \int d^3r n(\mathbf{r}) v(\mathbf{r}) \\ &= F_{LL}[n] + \int d^3r n(\mathbf{r}) v(\mathbf{r}) \end{aligned}$$

Levy constrained search formulation

2) Search for the minimum over all densities of the energy functional

$$E_0[n_0] = \min_{n(\mathbf{r})} \left(F_{LL}[n] + \int d^3r n(\mathbf{r}) \right)$$

Where $n_0(\mathbf{r})$ is the minimising ground-state density.

Thus, the constrained search formulation extends the validity of the HK theorems to *N-representable* densities.